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Mineral Migration and Regeneration Reactions in the Two Phase Flow Experiment

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Abstract

Scientists look forward to developing of emerging carbon oxide reduction technology which by artificial injection methods of industrial carbon dioxide geological storage in deep saline aquifers or geological structures, and then inhibit carbon dioxide accumulated in the atmosphere or prevent generation of the greenhouse effect. In this case, by using core flooding test for simulation the physical properties of the two-phase fluid flow (saline and carbon dioxide) in deep saline aquifers, the loss of mineral composition and regeneration reactions can be understood. In the initial experiments, we used Berea sandstone for core flooding test. In addition, the specimen was detected by X-ray diffraction and Scanning Electron Microscopy (SEM) analysis during the period before and after the test, to understand whether mineral crystal phase and microstructure changes had been occurred. After the core flooding test, the specimens were detected by energy spectrum of elements and elemental distribution analysis, and the main elements were oxygen and silicon.

keywords: saline aquifer, greenhouse effect, two-phase flow, core flooding, crystal phase, microstructure

1. Introduction

In recent years, application of artificial injection of industrial carbon dioxide geological storage technique were generally carried out in the advanced countries, in order reducing accumulation of carbon dioxide in the atmosphere and inhibit occurrence of the greenhouse effect [1]. In most circumstances, the carbon dioxide storage sites belong to the deep brine layer. Understanding the physical properties of two-phase flow (salt water and carbon dioxide) in saline aquifer, regeneration and loss of mineral after

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injection CO_2 in the formation and physical properties of rock, it will help to predict storage capacity, fluid migration, and injectivity in geologic reservoirs. Additionally, the chemical reactivity of the rock matrix with CO_2 affects the transport properties of the rock pore. In this paper, the research team firstly developed a set of experiment method for carbon dioxide and brine transport for the two-phase flow measurement system [2]. The experimental design is shown in Figure 1. In the experiment, the system is capable of displacing saturated-water inside specimens with either liquid or supercritical CO_2 in order to simulate the transmission of two-phase flow in case of formation. Special effort was taken to circumvent capillary end-effects during a period of experiment. This effect generally occurs at the both ends of the rock core, where the capillary pressure abruptly changes between rock and the inlet/outlet interface. So easily occur errors in measured values, and the appropriate pipeline design will be able to alleviate this situation. According to the previous research, capillary end effects can never be entirely prevented and have to be corrected [3].

In order to explore the micro-structure of rock core, the X-ray diffraction(XRD) analysis of mineral and Scanning Electron Microscopy analysis of mineral were used. To understand the core sample changes during before and after flooding test, the loss of minerals and regeneration reactions in rock samples. Testing rock samples were taken from the Taiwan Western Foothills belt (Pliocene to Pleistocene strata), also used origin from the United States, Ohio, Berea sandstone as a specimen of standard test for comparison.

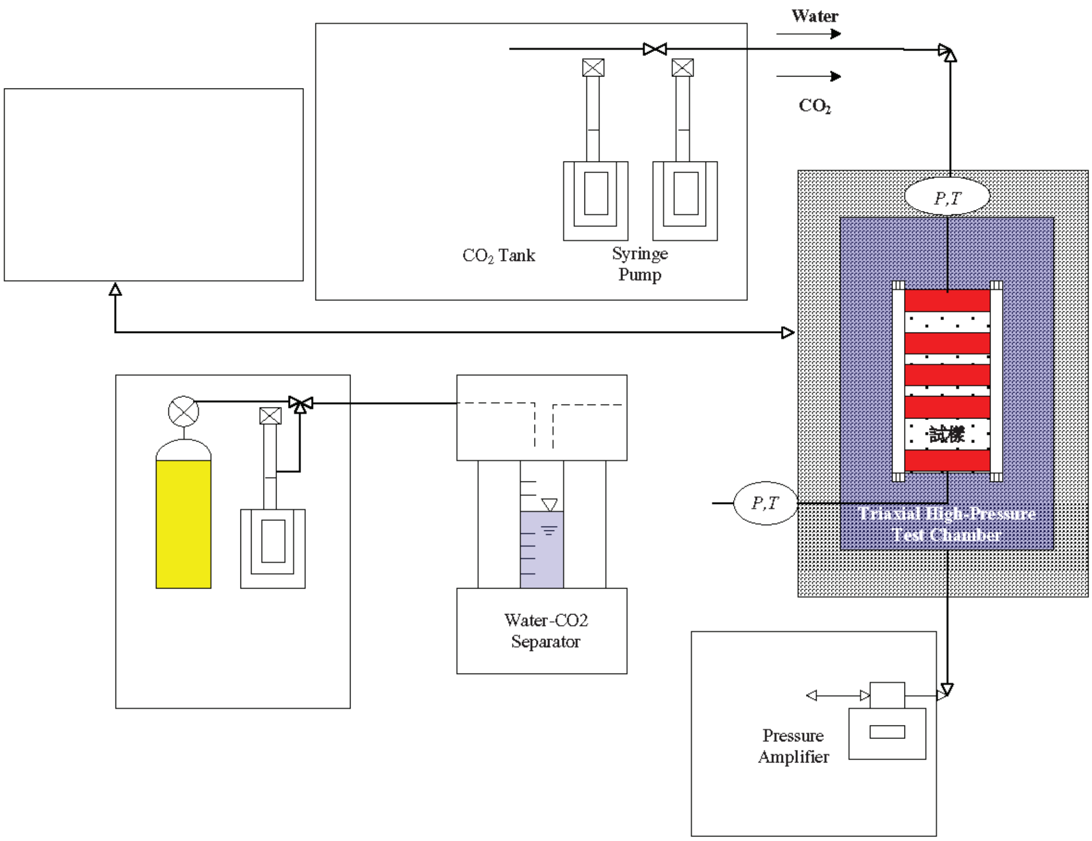

Fig.1. Schematic of the core flooding experimental apparatus

2. Samples

In the preliminary analysis, we used Berea sandstone for test, because there were consisted of sand-sized, SiO_2 by high purity quartz sand cemented, has a uniform composition features, and rock has visible laminations and can be easily split along the laminations structure. Each split of the rock can be regarded as a characteristic of a homogeneous material with very high porosity and high permeability, also easy to test analysis. we had obtained the permeability of Berea sandstone from core flooding test about 200 to 500 milidarcy. For the core flooding experiments, we used cylindrical specimens of 50 mm diameter and 50 mm length. For XRD and SEM detection technology, we used rough sliced specimens about 5 mm square and 3 mm thick for test.

3. Methodology

3.1. X-ray diffraction analysis of mineral

In order to affirm the mineral phase of specimen in this study. we used RIGAKU/DMX-2200 X-ray diffraction (XRD) facility to test. Experimental specimens of rock during before and after the two-phase flow test which were made for our rock samples by appropriate cutting, then the specimen was fixed and flattened with a glass plate on microscope stage. The instrument operated at 40 kV and 30 mA, using Cu K radiation. The speed of scanning is four degrees per minute, and the signal interval was 0.01 seconds. X-ray diffraction patterns were obtained in the 2 range between 5° ~ 65°. The measurement data used by the MDI JADE 5.0 software and publication of International Center for Diffraction Data (ICDD) , which is the original Joint Committee on Powder Diffraction Standard (JCPDS) published Powder Diffraction Files (PDF) [4] could be used together for identification analysis of crystalline phase.

3.2. SEM analysis of mineral

SEM analysis of the observed specimen microstructure in two-phase flow during period of before and after test, we used JEOL model JSM-6510 scanning electron microscope for test. Using principle of thermionic emission for emitting an electron beam through a set of condenser lens focusing, and selected the size of condenser aperture to control the diameter of electron beams, followed by a group controls of the electron beam scanning coils, and then focused through the objective lens, shooting in the specimen finally. The detection of signal will capture the secondary electron or backscattered electron to be an imaging. The apparatus was also installed Energy Dispersive Spectrometer (EDS) for semi-quantitative elemental analysis. At first, the specimen was set on stage by carbon tape for conductive fixed, then plated with gold or platinum by physical vapor deposition method to promote the electric conductivity of specimen. The microstructure and elemental analysis of specimen was observed by this apparatus. The facility operated at voltage of 15 kV, and a working distance of 12 mm.

4. The results of experiment

In order to further research the reactions in the specimen after the core flooding test, we had prepared sliced specimens which cut from a part of specimen by core flooding test, and the results were mainly obtained from the XRD and SEM analysis.

4.1. The results of XRD analysis

At first, we took the specimen from Berea sandstone before the two-phase flow test for XRD analysis, the data of experiment according to the published from the PDF2 item card of JCPDS (card number PDF # 99-0088) for identification. The results show main crystalline phase of specimen was quartz, and crystal faces of (011) direction its strongest diffraction peak. The angles of main diffraction with the corresponding relations produced the index of diffraction peaks, as shown in Table 1. The XRD results comparison chart which rock specimens during before and after test, as shown in Figure 2. The results indicated that Berea sandstone core samples by two-phase flow test had not accruing of new phases, the chemical composition of SiO_2 was still the quartz facies of hexagonal system.

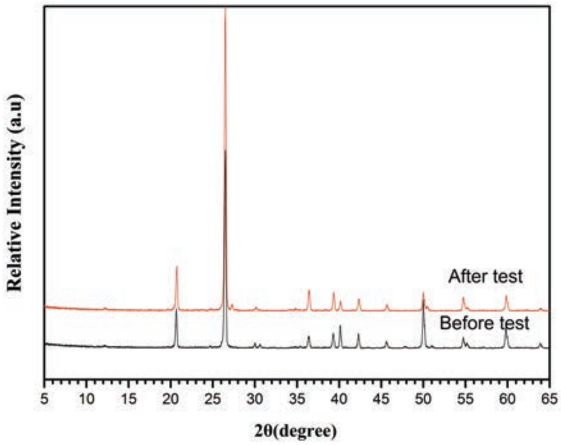

Fig.2. Berea sandstone specimens before and after test diffraction pattern

Table 1. The relationship of the main diffraction angles and corresponding to the diffraction crystal faces

Diffraction angle (2θ)	Miller indices of diffraction peaks (hkl)	Diffraction angle (2)	Miller indices of diffraction peaks (hkl)
20.859	(100)	50.140	(112)
26.640	(011)	50.621	(003)
36.546	(110)	54.874	(022)
39.467	(102)	55.326	(013)
40.219	(111)	57.233	(210)
42.452	(200)	59.960	(212)
45.795	(210)	64.034	(113)

4.2. The results of SEM analysis

Microstructure and Surface morphology of materials were recorded by scanning electron microscopy techniques to observe the changes between before and after core flooding test. The main principles of detection used electron beam focused on the specimen, meanwhile the electron of atom near surface of specimen released by collision of electron beams. It's an energy transfer mechanism (about 50eV) and newly generated electrons were called secondary electrons. In most statuses, the secondary electrons were detected had a chance of depart from the specimen surface under the surface of specimen about 5~50nm. These electrons attached with the message of the surface topography. While the electrons were received by detector, it will obtain images of the surface structure of specimen [5].

In the results of SEM analysis, we found the case can clearly see the surface of test specimens no significant structural change during the period of before and after test at 100 times magnification. At magnification 500 times, rock samples can be observed clearly in the pre-testing. There are a number of cuttings or fine particles of mineral absorption or agglomerate on the crystal particles of main mineral. At 6000 times the magnification, it also can be observed the same phenomenon. In contrast, the test image of 500 times or 6000 times magnification can be clearly comparison situation of adsorption on the minerals at the main debris or a sign of decrease of fine mineral particles in the after testing, as shown in Figure 3.

To better understand the specimen surface distribution of elements, we installed Energy Dispersive Spectrometer (EDS) instrument on SEM analyzer for test. The signals were detected by detector were the main characteristic spectrums of X-ray of element. The characteristic spectrums of X-ray were generated from the process of inelastic collision between high energy electrons and atoms of specimen. The incident electron beam caused to release electrons from the inner orbital, and the electrons of outer orbital fall into the low energy level orbital further generated characteristic of X-ray or Auger electrons. Therefore, variation of surface energy and wavelength were measured which can be determined elemental composition. Before the two-phase flow testing, the specimens were detected by EDS elemental analyzer at 500 times magnification. The detection element distribution mapping is shown in Figure 4, it can be found that the area with a large amount of white dots represents higher element concentration, hence the sample is contained components of carbon, oxygen, aluminum, silicon, sulfur, potassium, calcium and platinum in which oxygen, aluminum, silicon content is the highest. The source may come from the silicon dioxide (SiO_2) and a small amount of solid solution of aluminium oxide (Al_2O_3). Meanwhile, platinum should be plated on the specimen by machine before specimen pre-processing, it will promote the specimens conductivity to improve resolution of SEM image. Before the high-pressure supercritical carbon dioxide core flooding test, the results from the specimen were detected by testing apparatus which had been found silicon and oxygen elements energy reflection variation of intensity were the strongest, as shown in Figure 5.

After core flooding test, the elemental distribution mapping didn't find out calcium elements of signal, as shown in Figure 6. Compared to pre-testing results, there is no detection to others such as aluminum (Al) and potassium (K) elements of signal of the energy spectrum. For the technology of EDS detection, the element content of specimen should be detected more than 0.1wt%. So we can interpret by the two-phase flow test, fine-grained mineral particles or debris by adsorption or agglomerate on the original main mineral has been a significant reduction in the case, residual content should be less than 0.1wt% or less, as shown in Figure 7.

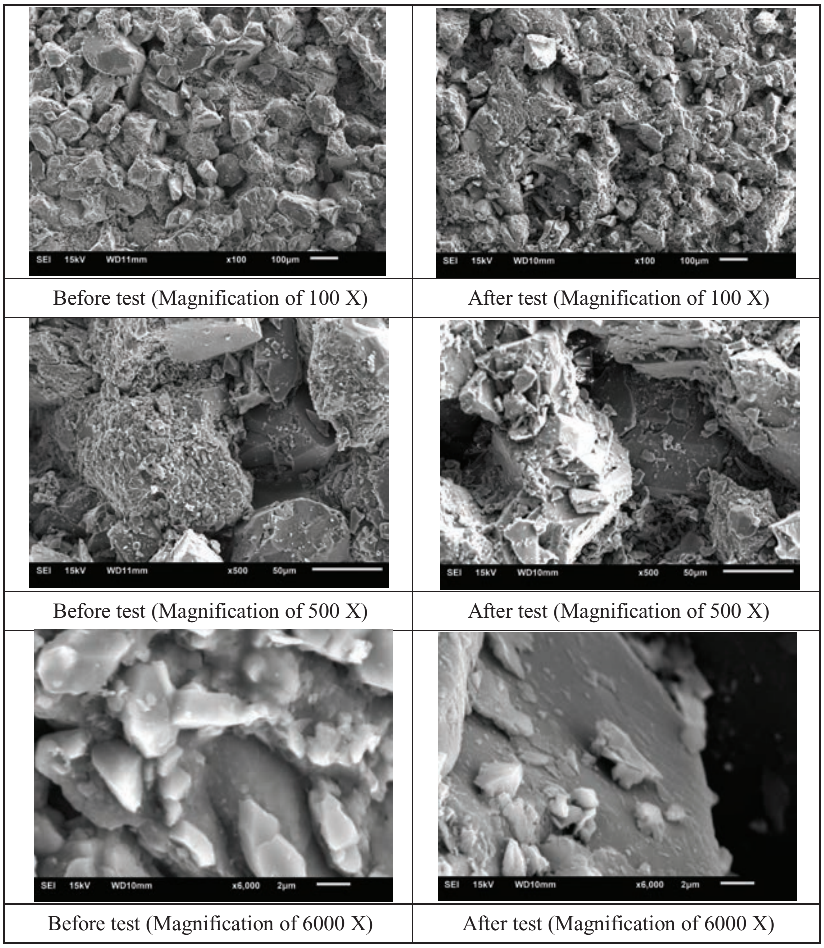

Fig.3. Secondary electron microscopy images of Berea sandstone

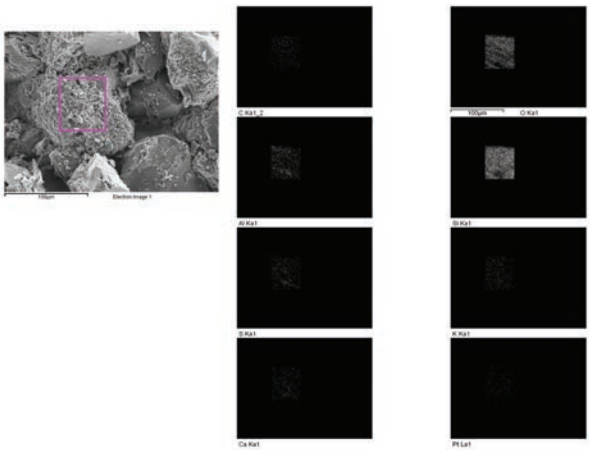

Fig.4. EDS elemental distribution analysis mapping of Berea sandstone before test

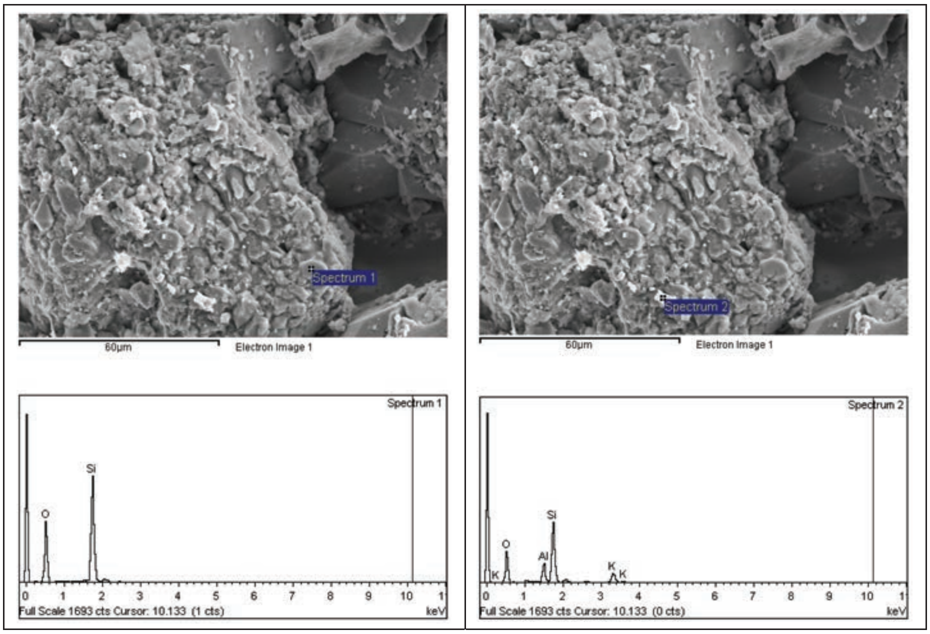

Fig.5. Elemental energy spectrum analysis of Berea sandstone before test

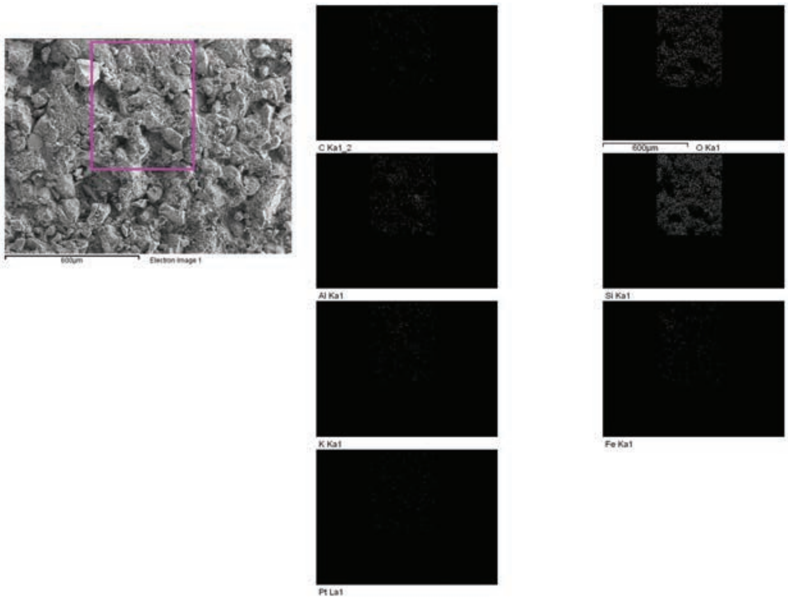

Fig.6. EDS elemental distribution analysis mapping of Berea sandstone after test

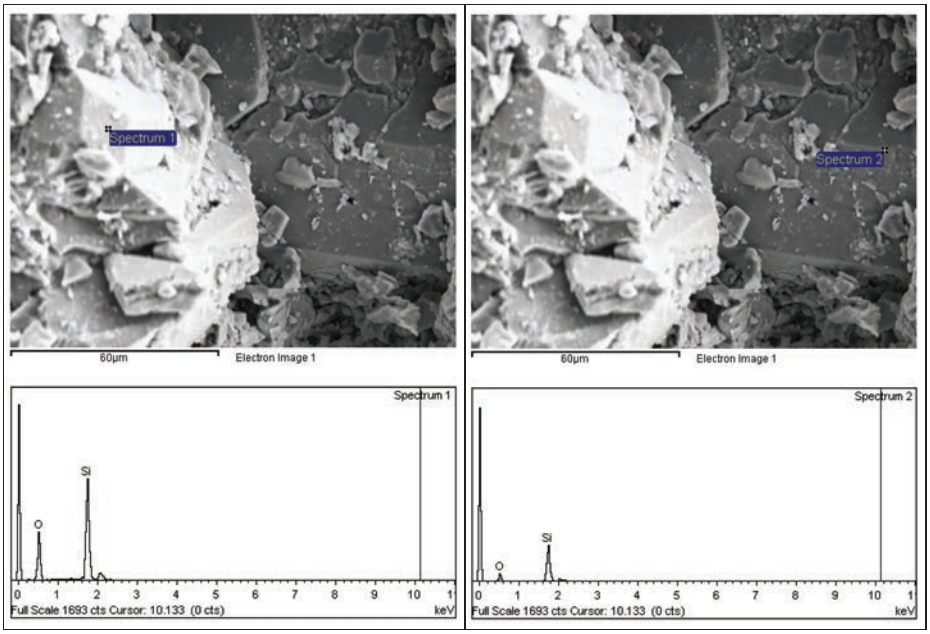

Fig.7. Elemental energy spectrum analysis of Berea sandstone after test

5. Conclusion

From the above experimental conclusion, the Berea sandstone by the XRD experiment results showing the main components of Berea sandstone were quartz mineral which were mainly consisted of silicon dioxide in silicate-based. By EDS technique to detect the other elements may be presented in the form of Substitutional Solid Solution which were existed in crystal of silicon dioxide. It was a result of quartz was formed in the process of diagenesis, and the Si^{4+} was replaced by Al^{3+} and Fe^{3+} in the silicate crystal. Because of relativity of displacement was low, therefore, none of new phase of Berea sandstone was formed. The Ca^{2+} should origin from minor cement, and Ca^{2+} of specimen was washed away from pore of rock by core flooding test. We can interpret specimens of the after core flooding test which were detected by energy spectrum of elements and elemental distribution analysis, the primary elements were oxygen and silicon, and no signals of calcium were detected.

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